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(71)Applicant : KAWASAKI STEEL CORP

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(72)Inventor : NAKAKOJI NAOMASA  
SHIGEKUNI TOMOFUMI  
KATO CHIAKI

### (54) POLYESTER RESIN-COATED TINNED STEEL SHEET

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a polyester resin-coated tinned steel sheet which has excellent adhesion with a polyester resin film, particularly, with a biaxial stretched polyethylene terephthalate film, and weldability without undergoing the incorporation of Cr which is regarded as an undesirable element from an environmental problem in spite of its action of improving the film characteristics of a chemical conversion film to be formed on the upper layer of a tin alloy layer.

SOLUTION: An intermediate layer formed on the surface of the steel sheet is provided with a tinned layer formed so that the intermediate layer is exposed to the surface in an area ratio of  $\geq 3.0\%$ . The surfaces of the exposed part of the intermediate layer and the tinned layer are provided with a chemical conversion film containing P of 0.5 to 100 mg/m<sup>2</sup> and Si of 0.1 to 250 mg/m<sup>2</sup>. The surface of the chemical conversion film is provided with a polyester resin coating laminated via a thermosetting adhesive.

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CLAIMS

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[Claim(s)]

[Claim 1] The polyester resin covering tin plated steel plate characterized by having the tinning layer formed on the interlayer who formed in the steel plate front face so that this interlayer might expose to a front face at 3.0% or more of rate of area, having the chemical film which contains Si of 0.5 - 100 2 mg/mP and 0.1 - 250 mg/m2 on an interlayer's surface exposure part and a tinning layer, and having polyester resin covering laminated through thermosetting adhesive on the front face of said chemical film.

[Claim 2] Said chemical film is a polyester resin covering tin plated steel plate according to claim 1 formed with the chemical conversion liquid containing P and a silane coupling agent.

[Claim 3] Said interlayer is a polyester resin covering tin plated steel plate according to claim 1 or 2 which is a Fe-Sn-nickel alloy layer or a Fe-Sn alloy layer.

[Claim 4] Said interlayer is a polyester resin covering tin plated steel plate according to claim 1 or 2 which consists of a Fe-nickel alloy layer which makes nickel/(Fe+nickel) mass ratio the range of 0.02-0.50, and a Fe-Sn-nickel alloy layer formed in the top face of this Fe-nickel alloy layer.

[Claim 5] The coating weight of a tinning layer is a polyester resin covering tin plated steel plate given in any 1 term of claims 1-4 which are 0.05 - 2.0 g/m2.

[Claim 6] A polyester resin covering tin-plated steel plate given in any 1 term of claims 2-5 characterized by said silane-coupling agent having an epoxy group.

[Claim 7] A polyester resin covering tin plated steel plate given in any 1 term of claims 1-6 said whose polyester resin covering is biaxial-stretching polyethylene terephthalate covering.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the polyester resin covering tin plated steel plate which carried out lamination covering of the film of polyester resin like biaxial-stretching polyethylene terephthalate with thermosetting adhesive especially about the surface treated steel sheet for cans used for a food can, a drink can, a common can, etc.

[0002]

[Description of the Prior Art] In order to have carried out canning of a food can, a drink can, the common can, etc. conventionally, the surface treated steel sheet which painted to the tin plated steel plate or the thin chrome plating steel plate was used. Paint is performed two or more times in many cases, the facility which processes an abandonment solvent since most coatings which the baking process of a coating is not only complicated, but uses for paint are the organic solvents which may cause a pollution problem by emission to atmospheric air is needed, and there is a problem that a facility cost burden becomes large. Moreover, in order to make it not use the coating of an organic solvent, the water coating is also developed, but since the paint film engine performance is inferior, the present condition is having not reached utilization level.

[0003] In order to solve these troubles, many attempts which laminate a thermoplastic resin film are made, and examination which laminates the film of polyester resin, such as a film of polyolefin resin, such as polyethylene resin and polypropylene resin, and polyethylene terephthalate resin, was performed. In these, the polyester resin film and the resin covering surface treated steel sheet which used thermosetting adhesive and laminated the biaxial-stretching polyethylene terephthalate film in the tin plated steel plate or the thin chrome plating steel plate especially are promptly put in practical use from excelling in the adhesion of a film.

[0004] As a steel plate which laminated the polyester resin film using thermosetting adhesive, although JP,63-13829,B, JP,4-74176,B, JP,5-71035,B, etc. are known, for example, each resin covering steel plate currently indicated by these is the same well-known surface treated steel sheet for cans as having been used for the conventional coated can.

[0005] As a typical surface treated steel sheet for cans, there are the tin plated steel plate and thin chrome plating steel plate which are called a tin plate from the former. In a tin plated steel plate Usually, it is common to form the chromate film which consists of a chromic-acid ghost, or a chromium metal and a chromic-acid ghost by electrolyzing in immersion or this solution into the water solution using the chromium compound of 6 \*\*, such as dichromic acid and a chromic acid, after performing tinning to a tin plate negative. Moreover, a thin chrome plating steel plate makes the layer which consists the same negative of a chromium metal and a chromic-acid ghost by electrolysis processing in the water solution of a chromic acid form. A chromic-acid ghost is shown in the maximum surface of the surface treated steel sheet for these cans, and it is known that this chromic-acid ghost has the operation which raises adhesion with a polyester resin film, especially a biaxial-stretching polyethylene terephthalate film.

[0006] However, when the safety reservation on work environment and waste water treatment not only

take great costs, but [ when the water solution using the chromium compound of 6 \*\*, such as dichromic acid and a chromic acid performs immersion processing or electrolysis processing, ] chromate treatment liquid should be revealed in accident etc., the danger of doing serious damage to an environment is large. From the environmental problem of these days, the motion which regulates chromium is advancing in each field, and the need for the chemical conversion which raises adhesion with a polyester resin film is increasing, without using chromium also in the surface treated steel sheet for cans.

[0007] As a technique about the chemical conversion replaced with the chromate treatment of the surface treated steel sheet for cans To JP,55-24516,B for example, by carrying out direct-current electrolysis in a phosphoric-acid system solution, using a tin plated steel plate as cathode The surface treatment method of the tin plated steel plate in which the chemical film which does not contain Cr was formed on the tin plated steel plate is indicated. To JP,1-32308,B The electroplating tin plate for seamless cans which gave the chemical film which is made to contain P, or P and aluminum in a chemical film, and does not contain Cr to the tinning layer front face is indicated.

[0008] However, in a lamination with a polyester resin film, no chemical films indicated by the supra official report can say that adhesion is fully acquired compared with the chromate film formed with conventional dichromic acid and a conventional chromic-acid solution.

[0009]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the polyester resin covering tin plated steel plate excellent in adhesion with a polyester resin film, especially a biaxial-stretching polyethylene terephthalate film, without making Cr made not desirable from the problem on an environment contain, although it has the operation which raises that coat property in the chemical film formed in the upper layer of a tinning layer.

[0010]

[Means for Solving the Problem] This invention is explained further below at a detail. When the chemical film which uses the above-mentioned conventional technique for the upper layer of a tinning layer, and does not contain Cr was formed, it was difficult to satisfy adhesion with a polyester resin film.

[0011] For this reason, artificers found out that sufficient adhesion with a polyester resin film could be satisfied, when it formed so that 3% or more of interlayer's part may more specifically be exposed to a front face at the rate of area, some interlayers who were formed in that lower layer in the tinning layer as a result of repeating research wholeheartedly that the above-mentioned technical problem in a surface treated steel sheet should be solved and who have the outstanding adhesion with said chemical film, and.

[0012] It turned out that the reaction radical which exists in this silane coupling agent will carry out orientation, and will more specifically contribute to adhesion greatly with the chemical conversion liquid which contains P and a silane coupling agent preferably at the upper layer of an interlayer's surface exposure part and a tinning layer if the chemical film containing a proper quantity of P and Si is formed.

[0013] The surface treated steel sheet of this invention therefore, on the interlayer who formed in the steel plate front face It has the tinning layer formed so that this interlayer might expose to a front face at 3.0% or more of rate of area. On an interlayer's surface exposure part and a tinning layer preferably It has a chemical film containing Si of 0.5 - 100 2 mg/mP and 0.1 formed with the chemical conversion liquid containing P and a silane coupling agent - 250 mg/m2. It is in having polyester resin covering laminated through thermosetting adhesive on the front face of said chemical film. In addition, as for the Si/P ratio in a chemical film (mass ratio), it is desirable to make it the range of 0.05-100.

[0014] Moreover, as for said interlayer, it is desirable that they are a Fe-Sn-nickel alloy layer or a Fe-Sn alloy layer, and it is more desirable to consist of a Fe-nickel alloy layer to which said interlayer makes nickel/(Fe+nickel) mass ratio the range of 0.02-0.50, and a Fe-Sn-nickel alloy layer formed in the top face of this Fe-nickel alloy layer. Furthermore, as for the coating weight of a tinning layer, it is desirable that it is 0.05 - 2.0 g/m2. It is more suitable that said silane coupling agent has an epoxy group further again. In addition, it is desirable that said polyester resin covering is biaxial-stretching polyethylene

terephthalate covering.

[0015]

[Embodiment of the Invention] The operation gestalt of this invention is explained below at a detail. The polyester resin covering tin plated steel plate of this invention It has the tinning layer formed on the interlayer who formed in the steel plate front face so that this interlayer might expose to a front face at 3.0% or more of rate of area. It has the chemical film which contains Si of 0.5 - 100 2 mg/mP and 0.1 - 250 mg/m2 on an interlayer's surface exposure part and a tinning layer. It is what has polyester resin covering laminated through thermosetting adhesive on the front face of said chemical film. Said interlayer It is the monolayer of a Fe-Sn-nickel alloy layer or a Fe-Sn alloy layer, or consists of compound layers of the Fe-nickel alloy layer which makes nickel/(Fe+nickel) mass ratio the range of 0.02-0.50, and the Fe-Sn-nickel alloy layer formed in the top face of this Fe-nickel alloy layer.

[0016] If a storage time until it is used since surface [ most ] is Metals Sn, although it remains as it is or general heat-treatment (reflow processing) for carrying out heating fusion of the Sn is performed (a Fe-Sn alloy layer will be formed between a tin plate negative and Sn plating layer in this case.) after the usual tin plate carries out Sn plating at a tin plate negative is long, Sn oxide will grow on the front face of Metal Sn. Since this Sn oxide is weak, it worsens film adhesion remarkably that it is easy to produce film exfoliation after a lamination with this Sn oxide as the starting point.

[0017] In order to solve this fault, it was coped with by performing chromate treatment conventionally, but even if it performs chromate treatment, growth of Sn oxide which tends to be produced on the front face of Metal Sn cannot be controlled completely.

[0018] Then, while acquiring the adhesion which was excellent with the surface exposure part of an interlayer without Sn oxide growth, the improvement effectiveness in weldability which tin has by the tinning layer is maintainable [ it has the tinning layer formed in this invention so that an interlayer might expose to a front face at 3.0% or more of rate of area, and supposes that a predetermined chemical film is formed in the upper layer of an interlayer's surface exposure part and a tinning layer, and ] as it is with this.

[0019] Making Sn alloy completely with a ferrite by the heat-treatment after tinning, and considering as a Fe-Sn alloy layer as an approach of forming an interlayer, is used well. Moreover, if nickel system is pretreated on a ferrite front face in this case, a more precise Fe-Sn-nickel alloy layer will be obtained.

[0020] As nickel system pretreatment, nickel flash plate plating processing and nickel diffusion process heat-treated after nickel plating are used well.

[0021] Moreover, when it constitutes said interlayer from a monolayer of a Fe-Sn-nickel alloy layer or a Fe-Sn alloy layer, it is in the inclination to excel in coating adhesion and the corrosion resistance after paint. Since each crystal of said alloy layer is precise and continuous, this is presumed to be that from which the coating adhesion which the phosphoric acid salt coat and silane coat which are formed in the upper layer could also take homogeneity and a precise gestalt, consequently was excellent, and the corrosion resistance after paint are acquired.

[0022] Moreover, when it constitutes said interlayer from a compound layer of a Fe-nickel alloy layer and the Fe-Sn-nickel alloy layer formed in the top face, a lower layer Fe-nickel alloy layer is desirable from the point that it is precise and it makes continuous the crystal of the Fe-Sn-nickel alloy of the upper layer formed at the time of a reflow when nickel/(Fe+nickel) mass ratio is 0.02-0.50.

[0023] That is, it is because consist of a crystal of the shape of a Fe-Sn alloy subject's square pole, and a chemical film also becomes is also hard to be formed continuously, so the improvement effectiveness of film adhesion is small when nickel/(Fe+nickel) mass ratio is less than 0.02. On the other hand, when nickel/(Fe+nickel) mass ratio exceeds 0.50, it is because the crystallized state of a Fe-Sn-nickel alloy serves as a non-dense, a chemical film is not formed precisely, either, so the improvement effectiveness of film adhesion is small.

[0024] In addition, nickel/(Fe+nickel) mass ratio can perform the depth direction analysis of Fe and nickel by mu-AES (micro Auger electron spectroscopy), can integrate with each peak value and the multiplier value of a relative sensitivity coefficient to the depth, and can calculate them from integral value [ of nickel ]/(integral value of integral value +Fe of nickel).

[0025] Furthermore, as other formation approaches of an interlayer, it may not be based on the diffusion alloying reaction after plating, but an interlayer may be formed by performing Sn alloy plating using Sn plating liquid which made Fe ion and/or nickel ion contain.

[0026] In addition, although this invention has the tinning layer formed on the interlayer who formed in the steel plate front face so that this interlayer might expose to a front face at 3.0% or more of rate of area, this is because it is suitable for acquiring the adhesion of the outstanding polyester resin film as mentioned above. The adhesion of polyester resin films with an interlayer's exposure product enough at less than 3% is not acquired. Moreover, since there is an inclination for the improvement effectiveness in weldability by the tinning layer to fall when the rate of area of an interlayer's surface exposure part becomes high too much, it is desirable to make the upper limit of said rate of area into 90%.

[0027] Moreover, it is desirable that the coating weight of a tinning layer is the range of 0.05 - 2.0 g/m<sup>2</sup> in this invention. It is because there is a possibility that sufficient weldability may no longer be obtained when tin coating weight is less than two 0.05 g/m, and is because it exceeds, and they become cost quantity although \*\* and weldability are enough, so they are not desirable 2.0 g/m<sup>2</sup>. In addition, Sn coating weight can be measured by the surface analysis by the electrical quantity method or fluorescence X rays.

[0028] And in this invention, it has the chemical film which contains P and Si on an interlayer's surface exposure part and a tinning layer, and the content of P and Si in this chemical film is made into coating weight, respectively, and is made into the range of 0.5 - 100 mg/m<sup>2</sup> and 0.1 - 250 mg/m<sup>2</sup>.

[0029] (1) P content in a considering [ make P content in a chemical film into the coating weight, and ] - as range of 0.5 - 100 mg/m<sup>2</sup> chemical film needs to make it the coating weight and to consider as the range of 0.5-100mg/m<sup>2</sup>. In less than two 0.5 mg/m, adhesion is not fully acquired and it is because it exceeds, it becomes easy to produce a defect in a chemical film then and adhesion deteriorates 100 mg/m<sup>2</sup>. In addition, the surface analysis by fluorescence X rays performed measurement of P coating weight.

[0030] Moreover, as the formation approach of a chemical film of having made P containing, it is desirable to carry out by phosphoric-acid system chemical conversion for example, and it is more suitable to use [ phosphate / metal salts such as a phosphoric acid of 1 - 80 g/l, sodium phosphate, aluminium phosphate, and potassium phosphate, / 1 hydrogen ] it by phosphoric-acid ion conversion as a source of supply of P in chemical conversion liquid in this case.

[0031] In addition, in chemical conversion liquid, metal salts, such as a metal salt, SnCl<sub>2</sub>, FeCl<sub>2</sub>, NiCl<sub>2</sub>, SnSO<sub>4</sub>, FeSO<sub>4</sub>, NiSO<sub>4</sub>, etc., of Sn, Fe, and nickel, can be added suitably. [ for example, ] In this case, etching agents, such as oxidizing agents, such as a sodium chlorate and a nitrite, and fluorine ion, may be suitably added as an accelerator.

[0032] The chemical film which made P contain can be formed by immersing or electrolysis processing the steel plate which formed the tinning layer on the interlayer on the above-mentioned front face of a steel plate so that this interlayer might expose to a front face at 3.0% or more of rate of area at the above-mentioned phosphoric-acid system chemical conversion liquid.

[0033] (2) Make Si contained in a considering [ make Si content in a chemical film into the coating weight, and ] - as range of 0.1 - 250 mg/m<sup>2</sup> chemical film contain by the silane coupling agent made to contain in processing liquid preferably. The general chemistry type of a silane coupling agent is X-Si-OR<sub>2</sub> or <sub>3</sub> (OR: alkoxy group).

[0034] An alkoxy silyl radical (Si-OR) is hydrolyzed by water, and a silane coupling agent generates a silanol group, and sticks it by the dehydration condensation reaction with the OH radical of a surface of metal. Moreover, the reaction radical which hits X of a general chemistry type carries out orientation, and dissolves or combines with resin at the upper layer of a steel plate.

[0035] As a silane coupling agent, in addition, 3-methacryloxy propyl trimethoxysilane, 2-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, 3-glycidoxypentyltrimethoxysilane, N-2-(aminoethyl)3-aminopropyl trimethoxysilane, N-2(aminoethyl)3-aminopropyl methyl dimethoxysilane, 3-aminopropyl triethoxysilane, N-phenyl-3-aminopropyl trimethoxysilane, 3-mercapto propyl methoxysilane, 3-chloropropyltrimethoxysilane, Vinyltriethoxysilane, a vinyl tris (2-methoxyethoxy) silane, Although the

N-2(aminoethyl)3-aminopropyl trimethoxysilane in which the amino group exists, N-2-(aminoethyl)3-aminopropyl methyl dimethoxysilane, 3-aminopropyl triethoxysilane, etc. can be used 2-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane and 3-glycidoxypropyltrimethoxysilane to which an epoxy group exists in X of X-Si-OR<sub>2</sub> or <sub>3</sub> especially in the general chemistry type of a silane coupling agent are suitable. This is because it excels in the compatibility with thermosetting adhesive and reactivity which are used for a lamination with a biaxial-stretching polyethylene terephthalate film.

[0036] In this invention, the improvement effectiveness in adhesion makes coating weight of Si contained in a chemical film the range of 0.1 which appears notably - 250 mg/m<sup>2</sup>. 0.1 since the improvement effectiveness in adhesion is not fully acquired in case of less than two mg/m<sup>2</sup> -- it is -- moreover, 250 mg/m<sup>2</sup> -- exceeding -- coming out -- it is because unreacted Si component remains, so the improvement effectiveness in adhesion decreases (a silane coupling agent carries out self-condensation). In addition, the surface analysis by fluorescence X rays performed measurement of Si coating weight.

[0037] The chemical film which made P contain using the above-mentioned phosphoric-acid system chemical conversion liquid as the formation approach of the chemical film containing P and Si can be made to be able to form, and it can carry out by processing with the solution which diluted the silane coupling agent in water further. In addition, when a silane coupling agent is processed with the solution diluted in water and crawling occurs since surface wettability is bad, the solution diluted with alcohol can be used. For example, ethanol can be processed to homogeneity with the solution which used more than 50mass% and a silane coupling agent 0.5 - 20mass%, and used the remainder as water. What is necessary is for spreading, desiccation, or immersion processing of a solution just to perform processing using the solution containing a silane coupling agent.

[0038] Moreover, the chemical film which contains P and Si with 1 liquid can also be formed by making the phosphoric-acid system chemical conversion solution which is the formation approach of the chemical film containing P contain a silane coupling agent. In this case, it is desirable to make pH into the range of 1.5-5.5. That is, if pH of chemical conversion liquid is adjusted to the range of 1.5-5.5, a silane coupling agent can be dissolved in homogeneity into chemical conversion liquid, and the outstanding adhesion will be acquired. pH -- the above -- it is because there is an inclination for the improvement effectiveness in adhesion to no longer be acquired fully by it becoming difficult to make homogeneity dissolve a silane coupling agent in chemical conversion liquid as it is out of range.

[0039] Moreover, in this invention, it is required for the above-mentioned chemical conversion tin plated steel plate to have covering of the polyester resin laminated through thermosetting adhesive. As said polyester resin, it is desirable to, use biaxial-stretching polyethylene terephthalate for example. In addition, "biaxial-stretching polyethylene terephthalate" here means what extended the thin film which consists of a polycondensation object of ethylene glycol and a terephthalic acid to length and width 2 shaft orientations. The film obtained as said thin film by carrying out extrusion molding of said polycondensation object, for example from a T die is mentioned. Although especially the thickness of a thin film is not restricted, it is desirable that it is 5-50 micrometers. It is because it is because it is not desirable, and the effectiveness like \*\* will not be acquired even if it makes it thicker than 50 micrometers but the rise of cost will be caused, in order for a lamination activity to take time and effort when thin film thickness is too as thin as less than 5 micrometers.

[0040] Moreover, thermosetting adhesive is used for a lamination with the tin plated steel plate and polyester resin film which carried out chemical conversion in this invention. In addition, although it does not specify especially if "thermosetting adhesive" here serves as a macromolecule which has three-dimension-network structure by the crosslinking reaction of the low-molecular monomer and curing agent by heat With an epoxy resin, phenol resin, epoxy phenol resin, melamine resin, epoxy melamine resin, a urea resin, an epoxy urea resin, alkyd resin, polyester resin, etc. What is necessary is just to have one or more sorts in a hydroxyl group, a carboxyl group, a urethane group, an epoxy group, an amide group, and an ester group for an adhesion function.

[0041] What is necessary is just to constitute thermosetting adhesive so that what is necessary may be just to prepare in the tin plated steel plate top which carried out chemical conversion, or one side of a



polyester resin film or the adhesion sides of a tin plated steel plate and a polyester resin film which carried out chemical conversion and both may be pasted up between the tin plated steel plate which carried out chemical conversion, and a polyester resin film.

[0042] Thermosetting adhesive can be applied to the tin plated steel plate and/or polyester resin film which carried out chemical conversion of that which was changed into the solution condition with a suitable organic solvent or water with the roll coat or the spray coat, and can be formed on suitable temperature, the tin plated steel plate which carried out chemical conversion by making it dry at 50-180 degrees C preferably, and/or a polyester resin film. When performing adhesion with required for a lamination being 0.2 - 10.0 g/m<sup>2</sup>, the weight of the thermosetting adhesive after desiccation is desirable, and is 0.5 - 5.0 g/m<sup>2</sup> more preferably.

[0043] What is necessary is to heat a steel plate at 190-280 degrees C, and just to laminate by pushing and sticking polyester resin by pressure with a roll etc. so that thermosetting adhesive may serve as an adhesion interface, in order to laminate the tin plated steel plate and polyester resin film which carried out chemical conversion with thermosetting adhesive.

[0044] Next, an example of the concrete manufacture approach of a polyester resin covering tin plated steel plate according to this invention is explained. After performing Sn plating to the negative which performed the negative or nickel diffusion process which performed the usual tin plate negative or nickel flash plate plating processing, Performing heating melting (reflow) processing at the temperature more than the melting point (231.9 degrees C) of tin, making a part of Sn alloy with a ferrite, and forming an interlayer It forms so that an interlayer may expose a tinning layer to a front face at 3% or more of rate of area by adjustment of the flux conditions before reflow processing, and immersion processing performs chemical conversion succeedingly. In addition, in order to raise the reactivity of chemical conversion after reflow processing, about two 1C/dm cathode processing may be performed in the sodium-carbonate water solution of 15 g/l.

[0045] as chemical conversion liquid -- phosphoric-acid ion conversion -- the phosphoric acid of 1 - 80 g/l, and tin ion conversion -- the stannous chloride of 0.001 - 10 g/l, and the sodium chlorate of 0.1 - 1.0 g/l -- containing -- further -- a silane coupling agent -- 0.5 - 20.0mass% -- the added water solution is used.

[0046] As for the conditions of chemical conversion, it is desirable that make temperature into 40-80 degrees C, and they make processing (immersion) time amount 1 - 5 seconds. The surface treated steel sheet after chemical conversion is dried by 35-150-degree C warm air.

[0047] Moreover, after processing with the above-mentioned chemical conversion liquid which does not contain a silane coupling agent as an option which forms a chemical film, the silane coupling processing liquid for forming a silane coupling layer, for example, the solution which used more than 50mass% and a silane coupling agent 0.5 - 20mass%, and used the remainder as water for ethanol, is applied to homogeneity, and there is the approach of drying so that steel plate skin temperature may reach 50-150 degrees C.

[0048] Then, a polyester resin covering tin plated steel plate is manufactured by carrying out thermocompression bonding of the biaxial-stretching polyethylene terephthalate film with a thickness of 25 micrometers to the tin plated steel plate in which the chemical film was formed, through the solution-ized epoxy phenol system thermosetting resin by the organic solvent.

[0049] In addition, after applying said thermosetting resin to the field equivalent to an adhesion side with said steel plate of a biaxial-stretching polyethylene terephthalate film so that desiccation Shigekazu Ushiro may be set to 2g/m<sup>2</sup> by the roll coater, and making it dry it at 170 degrees C, said thermocompression bonding is performed by being stuck to said steel plate heated at 200 degrees C by pressure with a roll so that thermosetting resin may become the interface of said steel plate and said film.

[0050] The place mentioned above cannot be passed for an example of the operation gestalt of this invention to have been shown, but various modification can be added in a claim.

[0051]

[Example] Next, the example of this invention is explained to a detail below.

- The chemical film was made to form in the surface treated steel sheet shown in Table 1 which made the tinning layer of the coating weight of per [ 0.05 ] one side - 2.0 g/m<sup>2</sup> form in the tin plate negative which consists of low-carbon steel of 0.1-1.0mm of one to example 12 board thickness, or super-low carbon steel with the application of either of four kinds of chemical conversion conditions (A-D). Then, the polyester resin film was laminated using either of three kinds of thermosetting adhesives (I, RO, Ha), and the polyester resin covering tin plated steel plate was manufactured. The presentation of a chemical film is shown in Table 1, and four kinds of chemical conversion conditions (A-D) are shown in Table 2, and thermosetting adhesive (I - Ha) is further shown in Table 3.

[0052] - the examples 1-5 of a comparison -- in addition, it manufactured in an interlayer's surface exposure moment list also about the surface treated steel sheet with either [ at least ] P in a chemical film, or the Si coating weight out of range proper [ this invention ] for the comparison.

[0053]

[Table 1]

	中間層		錫めっき層	化成処 理条件	化成皮膜		熱硬化性接着剤		ポリエステル樹脂被覆		評価結果
	組成	表面露出 面積率 (%)			P付着量 (mg/m <sup>2</sup> )	Si付着量 (mg/m <sup>2</sup> )	種類	乾燥重量 (g/m <sup>2</sup> )	ポリエステルの種類*	被覆厚み (μm)	
実施例1	Fe-Sn	20	1.20	A	7.5	11.50	イ	2.0	PET	25	3 6.5
実施例2	Fe-Sn-Ni	5	1.80	A	0.6	0.12	イ	1.0	PET	50	3 7.0
実施例3	Fe-Ni/Fe-Sn-Ni	88	0.09	B	12.0	15.00	ロ	0.5	PET	36	3 4.0
実施例4	Fe-Ni/Fe-Sn-Ni	30	0.85	C	22.0	20.00	ロ	5.0	PET	5	3 5.0
実施例5	Fe-Sn-Ni	40	0.65	D	36.0	145.00	イ	1.5	PET	10	3 5.0
実施例6	Fe-Sn	80	0.12	D	95.0	248.00	イ	2.5	PET	20	3 4.0
実施例7	Fe-Ni/Fe-Sn-Ni	4	1.90	B	15.0	18.00	ハ	3.0	PET	40	3 7.0
実施例8	Fe-Sn	15	1.10	D	45.0	95.00	イ	4.0	PET	25	3 6.5
実施例9	Fe-Ni/Fe-Sn-Ni	10	1.50	A	9.0	9.00	イ	3.5	PET	25	3 6.5
実施例10	Fe-Sn	93	0.08	A	8.5	10.00	ロ	0.8	PBT	50	2 4.0
実施例11	Fe-Sn	5	1.80	A	12.0	15.00	イ	0.1	PEN	25	2 7.0
実施例12	Fe-Sn-Ni	98	0.03	D	20.0	25.00	イ	1.0	PET	15	3 3.0
比較例1	Fe-Sn	12	1.50	B	0.4	0.25	ロ	0.5	PET	45	1 6.5
比較例2	Fe-Sn-Ni	20	1.20	C	1.0	0.07	ハ	2.5	PET	15	1 6.5
比較例3	Fe-Sn	35	0.70	B	110.0	6.00	ロ	7.5	PET	25	1 5.0
比較例4	Fe-Ni/Fe-Sn-Ni	10	1.70	D	55.0	260.00	ハ	4.5	PET	20	1 6.5
比較例5	Fe-Sn	2	2.20	C	3.0	8.00	ロ	0.3	PBT	30	1 7.0

(注) \* 1: PETは二軸延伸ポリエチレンテレフタレート、PBTはポリブチレンテレフタレート、PENはポリエチレンナフタレートを意味する。

[0054]  
[Table 2]

化成処理条件	化成処理液	処理方法												
A	りん酸 1~80 g/L シランカップリング剤(a)*注 0.5~20 mass% 塩化第一錫 0.001~10 g/L 塩素酸ナトリウム 0.1~1.0 g/L	浸漬処理												
B	りん酸 1~80 g/L シランカップリング剤(b)*注 0.5~20 mass% 塩化第一鉄 0.001~10 g/L 塩素酸ナトリウム 0.1~1.0 g/L	浸漬処理												
C	りん酸 1~80 g/L シランカップリング剤(c)*注 0.5~20 mass% 塩化ニッケル 0.001~10 g/L 塩素酸ナトリウム 0.1~1.0 g/L	電解処理												
D	<table><tr><td>りん酸</td><td>1~80 g/L</td></tr><tr><td>塩化第一錫</td><td>0.001~10 g/L</td></tr><tr><td>塩素酸ナトリウム</td><td>0.1~1.0 g/L</td></tr></table> <p style="text-align: center;">+</p> <table><tr><td>シランカップリング剤(d)*注</td><td>0.5~20 mass%</td></tr><tr><td>エタノール</td><td>50~99 mass%</td></tr><tr><td>水</td><td>0~1 mass%</td></tr></table>	りん酸	1~80 g/L	塩化第一錫	0.001~10 g/L	塩素酸ナトリウム	0.1~1.0 g/L	シランカップリング剤(d)*注	0.5~20 mass%	エタノール	50~99 mass%	水	0~1 mass%	浸漬処理  +  塗布処理
りん酸	1~80 g/L													
塩化第一錫	0.001~10 g/L													
塩素酸ナトリウム	0.1~1.0 g/L													
シランカップリング剤(d)*注	0.5~20 mass%													
エタノール	50~99 mass%													
水	0~1 mass%													

\*(注) シランカップリング剤(a): 3-グリッドキシアロビトリオキシシラン(エボキシ系)  
 シランカップリング剤(b): 2-(3,4-エボキシシクロヘキシル)エチルトリオキシシラン(エボキシ系)  
 シランカップリング剤(c): N-2-(アミノエチル)3-アミノプロピルトリオキシシラン(アミン系)  
 シランカップリング剤(d): ビニルトリエトキシシラン

[0055]

[Table 3]

	熱硬化性接着剤
イ	エポキシ-フェノール系
ロ	ポリエステル-イソシアネート系
ハ	水性エポキシ変性ポリエステル-水性メラミン系

[0056] (Performance evaluation) About each surface treated steel sheet of examples 1-12 and the examples 1-5 of a comparison, evaluation about the adhesion and weldability of a polyester resin film was performed.

[0057] (1) After fabricating by having \*\*\*\*ed so that a polyester resin film plane might be on a convex side only 5mm using an Erichsen tester, after putting a cross cut into a film adhesion test polyester resin covering tin plated steel plate and being immersed in ebullition underwater after that for 5 hours, the pincette tore off the polyester resin film from the cross-cut section, and the three-stage which shows the adhesion (does a film exfoliate or not?) of a film below according to an exfoliation situation estimated. The evaluation result is shown in Table 1.

(Adhesion evaluation) When a score 3= film does not exfoliate When a score 2= film exfoliates slightly It is [0058] when a score 1= film exfoliates. (2) The tin plated steel plate which carried out polyester resin covering except for the part (width of face of both ends: about 5mm) equivalent to a weldability test weld zone was fabricated in the shape of a cylinder, and weld zones were welded by the welding condition shown in superposition and Table 4 by width of face of 1mm. At this time, there is welding reinforcement with the amount of [ which was welded ] sufficient joint, the existence of the existence of the welding primary-current range (proper welding current range) which welding Chile moreover does not produce was investigated, when the proper welding current range existed, that current range was measured, and weldability was evaluated.

[0059]

[Table 4]

溶接条件

溶接機	Soudronic社製 銅ワイヤーシーム溶接
溶接速度	20m/min
溶接加圧力	637N(65kgf)

[0060] Examples 1-12 excelled [ each ] in the adhesion of a polyester resin film so that clearly from the result of Table 1. On the other hand, it turns out that the examples 1-5 of a comparison have the bad adhesion of a polyester resin film, and there are in practical use level. [ no ]

[0061]

[Effect of the Invention] Offer of the polyester resin covering tin plated steel plate excellent in adhesion and weldability with a polyester resin film, especially a biaxial-stretching polyethylene terephthalate film was enabled without making Cr made not desirable from the problem on an environment contain according to this invention, although it had the operation which raises that coat property in the chemical film formed in the upper layer of a tinning layer.

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[Translation done.]